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THE PRESENCE OF ARSENIC IN HOPS.

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SITUATION WITH RESPECT TO ARSENIC IN HOPS.

At times the detection of minute traces of arsenic in shipments of American hops exported to foreign countries has led to their rejection by prospective purchasers. The loss sustained in such cases is borne by the exporter; consequently American growers, who sell as a rule to local buyers only, do not realize fully the extent to which the salability of American hops on foreign markets may be affected unfavorably by an occasional contaminated shipment.

The profitableness of hop production in the United States is determined practically by the extent of the foreign demand for the crop surplus in excess of the requirements for domestic consumption. Any impairment of the quality of American hops, whether definitely proved or only suspected by foreign consumers, lessens the chances for marketing the surplus at reasonable prices and eventually reacts upon the grower in a lower price for his product. Although the probability of any damage to the public health from arsenic communicated by hops to ale or beer seems very remote, nevertheless the minute quantity of arsenic permissible in hops under some foreign standards of purity lays the grower under obligation to use every reasonable precaution to avoid all possible sources of contamination.

In a bulletin published in 1908 by the Bureau of Plant Industry,[1] impure sulphur was suggested as the source of the traces of arsenic

[1] Stockberger, W. W. The sources of arsenic in certain samples of dried hops. *In* U. S. Dept. Agr., Bur. Plant Indus. Bul. 121, p. 41-46. 1908.

occasionally found in American hops, and hop growers and handlers were urged to avoid the use of sulphur which could contaminate the hops in the process of drying and curing. Following this publication some hop growers made an effort to secure arsenic-free sulphur, but most of the growers on the Pacific coast continued to use impure sulphur, with the result that each year hops contaminated with arsenic have found their way into foreign markets. In the hops produced in the crop year 1914 the quantity of arsenic present was in many cases so much larger than usual that some English consumers brought the matter informally to the attention of the Bureau of Plant Industry and expressed the hope that American hop growers could be made to realize the seriousness of the situation from the standpoint of the foreign purchaser.

From an inquiry made among the hop growers of the Pacific coast it appeared that the sulphur in common use for bleaching hops was generally regarded either as free from arsenic or as containing this element in quantities so small that no injury would result from its use. The soil, commercial fertilizers, and materials used in spraying, rather than the sulphur, were all suggested as probable sources of the arsenic in hops, but on account of the prevailing uncertainty as to its real source little progress apparently was made in the production of hops of a quality more acceptable to the foreign trade. The reliability of the methods used for the determination of small quantities of arsenic in hops and similar materials was questioned by some who had given careful consideration to the subject. Therefore, the Bureau of Plant Industry and the Bureau of Chemistry undertook a joint investigation in order to establish definitely the source of the contamination of the hops. The field investigation and the collection of samples were made by the representative of the Bureau of Plant Industry, while the study of methods of analysis and the analyses of the samples collected were made in the Bureau of Chemistry.

COLLECTION OF MATERIALS FOR EXAMINATION.

The hop-producing sections of Oregon were visited during the hop harvest of 1915, and a carefully selected series of samples of both hops and sulphur was obtained. Definite information was in hand regarding the origin of certain bales of hops of the crop of 1914 which had been rejected by English purchasers, and it was therefore possible to locate the particular fields on which the hops in many of these bales were produced. It was possible also in some cases to locate and examine the kilns in which some of the rejected hops were dried and to secure samples of the sulphur used in their preparation.

Composite samples of hops from several fields were secured by taking a few hops from each of a number of vines in a field. These

samples were collected just before the crop was picked and were dried carefully in the open air, thus avoiding any possible chance of contamination from the sulphur. For comparison with the field samples thus prepared, samples of the hops from these fields, as well as samples of the sulphur used to bleach them, were taken at the kilns. Samples of kiln-dried hops and, when possible, samples of the sulphur used in bleaching them, were also secured from several widely separated localities. The soils on which these hops were produced varied from the alluvial sandy loam along the river to the clay loam of the uplands and represented practically all the soil types ordinarily used for the production of hops.

Some samples of Fuggle, an early variety, also were collected for comparison as to arsenic content with the later variety known as Cluster or English Cluster.

ANALYSIS OF MATERIALS.

Arsenic was determined by the modified Gutzeit method, following in general the procedure outlined by C. R. Smith.[1] A discussion of the method and of the reasons for adopting the exact details followed in this work will be published elsewhere.[2] The hops were treated with nitric and sulphuric acids to destroy organic matter. The sulphur was treated with bromin[3] and the arsenic separated from the sulphur bromid by extraction with bromin water. In all cases arsenic was precipitated as ammonium magnesium arsenate by adding microcosmic salt, magnesia mixture, and ammonia. The precipitate of phosphate and arsenate was dissolved in sulphuric or hydrochloric acid, the arsenic reduced by stannous chlorid, and arsin generated by the use of zinc. The arsin was allowed to pass over a strip of paper containing mercuric bromid, making a brown stain, the length of which depended upon the quantity of arsenic in the sample. When large quantities of arsenic were present the arsin was passed into a solution of mercuric chlorid; the precipitated mercurous chlorid was filtered on ignited asbestos in a Gooch crucible, dried, and weighed.

RESULTS OF ANALYSES.

The results of the analyses of the field samples, dried in the sun without contact with sulphur fumes, are given in Table I. Although these samples came from widely separated yards and represented two varieties of hops, little difference is shown in their arsenic content, which is uniformly small. The analysis of samples 176, 201, and 202,

[1] Smith, C. R. The determination of arsenic. U. S. Dept. Agr., Bur. Chem. Cir. 102, 12 p., 2 fig. 1912.

[2] Collins, W. D. C. R. Smith's method for the determination of arsenic (with special reference to the determination of arsenic in hops and in sulphur). Presented at the meeting of the Assoc. Off. Agr. Chem., Nov. 20–22, 1916. (To be published in Jour. Assoc. Off. Agr. Chem.)

[3] Smith, W. Estimation of selenium in sulfur. *In* Jour. Indus. and Engin. Chem., v. 7, no. 10, p. 849–850. 1915.

which were of the Fuggle variety, do not differ essentially from those of the remaining samples, which were of the English Cluster variety.

Samples 178 and 186, taken from yards which were not sprayed, showed practically the same quantity of arsenic as the samples from yards sprayed with a solution of whale-oil soap and quassia.

The quantities of arsenic found in the unsulphured samples were far below the limit of 0.01 grain per pound (1.4 parts per million) set in England by the Royal Commission on Arsenical Poisoning.

TABLE I.—*Arsenic in sun-dried unsulphured hops grown at Independence, Oreg., in 1915.*

No.	Source of sample.	Arsenic as As_2O_3 (part per million).	No.	Source of sample.	Arsenic as As_2O_3 (part per million).
176	Yard A	0.2	196	Yard G	0.2
177	do	.2	199	Yard H	.2
178	Yard B	.2	201	Yard I	.1
185	Yard C	.1	202	do	.1
186	Yard D	.1			
187	Yard E	.1		Average	.16
194	Yard F	.3			

The quantities of arsenic found in samples of sulphured hops are given in Table II. Where possible, samples of the sulphur used in curing these hops were collected and analyzed. The results of these analyses also are given in Table II.

Of the 26 samples of kiln-dried hops only four, of which two were duplicates, contained less than 1 part of arsenic per million parts of hops. The average results show that whereas unsulphured hops contain no appreciable quantity of arsenic, hops which were treated with fumes from sulphur having about 100 parts of arsenic (As_2O_3) per million contained about 3 or 4 parts of arsenic per million parts of hops.

On account of the irregularity of distribution of arsenic in the sulphur, it is not possible to be sure that any sample of hops was treated with sulphur of exactly the composition of the sample taken to represent the sulphur. The quantity of sulphur used is also variable, ranging from 1 to 4 pounds of sulphur for 25 pounds of dried hops. Notwithstanding all these chances for disagreement, the results in Table II show in general a relation between the quantities of arsenic in the hops and in the sulphur used in curing. The quantities of arsenic in the hops average about 3 or 4 per cent of the quantity in the sulphur used in curing. On this basis sulphur containing 25 or 30 parts of arsenic per million would on the average contaminate hops with about 1 part of arsenic per million parts of hops. If the arsenic is unevenly distributed through the sulphur it is possible that some samples of hops might contain much more arsenic than the quantity which would correspond to the arsenic in the sulphur.

TABLE II.—*Arsenic in kiln-dried hops and in sulphur used in curing certain lots of hops grown in Oregon in 1915.*

No.	Source of sample.		Arsenic as As_2O_3 (parts per million).		No.	Source of sample.		Arsenic as As_2O_3 (parts per million).	
	Place.	Yard, etc.	In the hops.	In the sulphur.		Place.	Yard, etc.	In the hops.	In the sulphur.
195	Independence	Yard G	0.4	20	208	Brooks	Yard B	0.5	4.4
229	do	Yard G (duplicates)	6.6	20	205	Springfield	Yard A	4.2	.....
233	do	Yard G (duplicates)	7.1	.....	210	do	Yard B	4.1	.....
198	do	Yard H	5.2	116	206	Harrisburg	Yard A	2.6	.....
180	do	Yard K	3.8	356	209	do	Yard B	4.5	.....
207	do	Yard L	1.0	.....	211	do	Yard C	26.0	.....
224	do	Yard M	6.1	35	212	Aurora	.....	3.4	115
228	do	Yard N (duplicates)	1.3	.....	214	Donald	Yard A	2.7	90
232	do	Yard N (duplicates)	1.2	.....	216	do	Yard B	3.4	123
230	do	Yard O (duplicates)	1.9	20	218	St. Paul	.....	3.8	116
234	do	Yard O (duplicates)	1.9	.....	223	Suver	.....	3.9	76
231	do	Yard P (duplicates)	.2	.....	225	Banks	.....	4.2	188
235	do	Yard P (duplicates)	.2	.....					
204	Brooks	Yard A	1.9	.....		Average	.....	3.93	.....

Analyses of all the samples of sulphur collected are given in Table III. With a few exceptions these samples were taken from the hop yards and are representative of the sulphur used in curing the crop of 1915. Three samples of sulphur used in curing the crop of 1914 and two commercial samples also are included.

The quantity of sulphur on hand at the hop kilns varied from a few hundred pounds to several tons. As a rule, the individual lots were far from uniform in appearance, and in many cases several different kinds of sulphur seemed to be present. Some pieces were of a bright lemon-yellow color and others of various shades of orange. Some pieces were hard and glasslike; others appeared more crystalline and crumbled readily, while some pieces were porous, resembling pumice in appearance. In most of the lots the sulphur consisted of pieces of different sizes, from lumps 6 or 8 inches across down to a fine powder. This made sampling difficult, but the agreement between the values obtained for samples 181 and 200, which were taken to represent the sulphur in one lot, indicates that the samples were representative of the various lots at the time of sampling.

TABLE III.—*Arsenic in sulphur used for curing hops grown in Oregon in 1915.*

No.	Source of sample.		Arsenic as As_2O_3 (parts per million).	No.	Source of sample.		Arsenic as As_2O_3 (parts per million).
	Place.	Yard, etc.			Place.	Yard, etc.	
182	Independence	Yard B	64	213	Aurora	.....	115
191	do	Yard F (1915)	197	215	Donald	Yard A	90
192	do	Yard F (1914)	170	217	do	Yard B	123
197	do	Yard H	116	219	St. Paul	.....	116
179	do	Yard K (1915)	66	220	Brooks	Yard B	4.4
181	do	Yard K (1914) (duplicates)	356	222	Suver	.....	76
200	do	Yard K (1914) (duplicates)	329	226	Banks	.....	188
221	do	Yard M	35	190	Independence	Commercial sample	3.6
193	do	Yard O	20	227	Portland	Dealer's sample	7.1
189	do	Yard R	141		Average	.....	116.7

From two samples of sulphur several pieces of different appearance were picked out, ground, and analyzed for arsenic, with the results given in Table IV.

TABLE IV.—*Arsenic in different pieces of sulphur from the same field sample.*

No.	Subsample.	Appearance.	Arsenic as As_2O_3 (parts per million).	No.	Subsample.	Appearance.	Arsenic as As_2O_3 (parts per million).
179	1	Greenish yellow	10	188	3	Lemon yellow, largely crystalline	160
179	2	Slightly orange, porous	270	188	4	Orange, vitreous	150
179	3	More orange than subsample 2	160	188	5	Lemon yellow, crystalline	50
179	4	Average of the sample	66	188	6	Orange, vitreous	450
188	1	Average color	35	188	7	do	300
188	2	do	80				

After a small part of sample 179 had been removed in subsamples 1, 2, and 3, the remainder was ground and used as an average sample of 179 in the same way in which the other samples of sulphur were used. It is believed that the average value of 66 parts per million is not appreciably different from that which would be obtained for the arsenic in sample 179 if no subsamples had been removed. So many subsamples of sample 188 were taken that it was not possible to obtain an average value of this sample.

The results of analyses of the subsamples of sample 179 indicate that with sulphur taken from a lot containing on the average 66 parts of arsenic per million, one kiln of hops might be treated with fumes from sulphur containing 270 parts of arsenic per million, while the next treatment might be with sulphur containing only 10 parts of arsenic per million.

Since only a small quantity of sulphur is burned at one time in curing hops, it is very probable that the sulphur used on a particular kiln of hops will not contain the same quantity of arsenic as an average sample of the sulphur on hand.

The results for the subsamples of sample 188 show irregularity of distribution of arsenic much like that in sample 179. The relation between the arsenic in sulphur and in the hops for which the sulphur is used can not be very definite. No uniform quantity of sulphur is used for a given quantity of hops; the arsenic is not uniformly distributed through the hops in the kiln at one time and the arsenic is not uniformly distributed through the sulphur.

The analyses of samples 190, 220, and 227 show that sulphur can be obtained which is practically free from arsenic. The analyses of samples of hops cured with sulphur containing very little arsenic indicate that hops may be cured with sulphur containing as much as 10 parts of arsenic per million without becoming contaminated with more than 0.5 part of arsenic per million parts of hops.

CONCLUSIONS.

The work here reported shows that sun-dried hops collected from various yards in Oregon in 1915 contained practically no arsenic.

The spraying materials in general use, such as solutions of whale-oil soap and quassia or nicotin sulphate are not to be held responsible for the contamination of hops with arsenic.

The sulphur in use in 1914 and 1915 was generally contaminated with arsenic, many samples containing over 100 parts of arsenic as As_2O_3 in 1,000,000 parts of sulphur. When such sulphur is used in curing hops, the hops may contain three or four parts of arsenic per million parts of hops.

Little, if any, doubt remains that impure sulphur alone is responsible for the contamination of hops with appreciable quantities of arsenic.

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